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(54) **Process for treatment of oils and fats and products so obtained**

(57) Process for treatment of an oil or fat, animal or vegetal, raw, semi-processed or refined, consisting of adding to such oil or fat at least one enzyme allowing to hydrolyze and/or depolymerize the non-glyceridic compounds contained therein.

"Process for treatment of oils and fats and the products so obtained"

This invention concerns a biological treatment process for oils and fats, animal or vegetal, raw, semi-processed or refined, as well as the oils and fats so obtained.

It is well-known that almost all oils and fats contain non-lipids and phosphatides in solution or suspension. For simplicity, the terms "non-lipids" and "phosphatides" will be included hereinafter under the more general term of "non-glycerides," following in this regard the classification of "Bailey's Industrial Oil & Fat Products" 4th edition, 1980, Volume 1, pages 45 to 83, published by Daniel SWERN, Wiley Interscience Publication, New York USA. These may be present in large quantities, as for example in clarified butter, illipe oil, certain oils of fish and marine mammals, such as spermaceti, certain raw animal oils and fats such as dehydrated butter, chicken fat, etc.; but often these non-glycerides are found in low concentration, or even traces, but nevertheless presenting a marked inhibitory effect on processing (for example a negative effect on crystallization) or interfering

with the final products (for example, a negative effect on oil clarification), as may be the case for sunflower, cotton, olive cake oils, etc.

It is well-known that the "impurities" of processed oils have a negative action on refining operations and yields, which is the reason that neutralization or deacidification of the oils is generally preceded by prior "degumming." Equally, in fractionation by crystallization, the presence of non-glycerides may have, even in traces, a significant inhibitory effect on the crystallization of oils and fats.

Consequently, these non-glyceridic and often inhibitory substances contained in oils and fats, especially in raw oils, include, first of all, the phosphatides. Phosphatides, among which the most common ones are lecithins and cephalins, are triglycerides in which one of the acyl radicals (-CO-R) is substituted by phosphoric acid, itself saturated by a basic group, for example choline or cholamine. Phosphatides have a well-known emulsifying and anticrystallizing power.

Among the non-lipids contained in oils and fats, we can point out:
- carbohydrates or glucides, included in two main groups, monosaccharides and polysaccharides. Monosaccharides, such as glucose, glactose, etc. are generally present

in oils and fats in the form of sugar-phospholipid complexes (for example inositol which is a combination of phosphatide and galactose, or phytosteroline, composed of phytosterol and glucose). Polysaccharides, mainly polyholosides (gums, cellulose, ...), as high polymers, are insoluble in water or provide colloidal solutions. These polysaccharides may be hydrolyzed to complete degradation into monosaccharides. Some of them are soluble in hot water (glycogen, amidon, pectin) but may form gelatinous masses;

- certain simple (gelatin) and compound (casein) proteins as well as certain degradation products (peptones, proteoses) which may be found solubilized in oils and fats, in particular if the oleaginous grains and fruits or the animal tissues from which they originate have been damaged by hydrolytic decomposition prior to their extraction;
- certain resins, waxes, latex and various mucilages;
- sterols of all types;
- carotenoid pigments, etc.

Although most of the phosphatides and non-lipids in general found in oils and fats are eliminated after neutralization with alkalis, these substances foreign to oil or fat itself interfere with the efficacy of these treatments, especially after centrifugation, filtration, crystallization, fractionation, winterization and clarification operations.

One of the essential purposes of this invention consists of remedying the aforementioned shortcoming of existing oils and fats, and establishing an industrially and economically valid process which allows obtaining oils and fats significantly "cleaner" and with lower viscosity than the oils and fats processed according to classic processes, especially after the various operations mentioned above, to which oils and fats are subjected.

For this purpose, the process according to the invention consists of adding to the oil or fat to be processed, at least one enzyme which hydrolyzes and/or depolymerizes the non-glyceridic compounds contained therein.

According to one particular embodiment of the process under the invention, the enzyme is added before the operations of centrifugation, filtration, crystallization, fractionation, winterization or clarification of this oil or fat.

According to one particularly preferred embodiment of the invention, the enzyme is chosen from the group which includes phosphatases, pectinases, cellulases, amylases, gumases, proteases and mixtures of two or more of these substances.

Another object of the invention are the oils and fats obtained by the process described above.

Other details and particularities of the invention will emerge from the description given below, as an example, without limitation thereof, of some particular forms of the invention.

As it results from the above, this invention proposes to previously process oils and fats, by the appropriate enzymes, so as to significantly improve the conditions in operations such as centrifugation, filtration, crystallization, fractionation, winterization or clarification. Thus, if the crystallization conditions of an oil or fat are significantly improved, filtration conditions are automatically improved, or such filtration is simply made possible. Equally, although good crystallization is capital, in winterization and fractionation, it mainly depends on the "cleanliness" of the processed oil. Fractionation is progressive cooling (winterization) of a fat, followed by separation of the crystals, in order to obtain two different fatty phases. Winterization is the winterization of a liquid oil, followed by separation of the crystals, in order to obtain, by filtration or centrifugation, a main clear phase. Among industrial winterization and fractionation processes, the crystallization and filtration processes described in Belgian patents No. 713,430 and No. 713,330, for example, are cited. Clarification is an oil polishing operation, retaining the turbidity, impurities and minicrystals present in the oils, on filtering surfaces, so as to render them clear and shiny.

Enzymes are proteins with powerful

and very selective catalytic effect. In fact, each enzyme has the property of specifically catalyzing one organic reaction via the formation of an enzyme-substrate complex. It has thus been found, according to the invention, that a certain number of enzymes specifically attack non-glyceridic compounds of various oils and fats, due to the very nature of this compound.

Among enzymes specifically active in this area, are noted, particularly, phosphatases (phospholipases-C), which attack phosphatides: pectinases, celulases, amylases, specifically different carbohydrates; gumases, specific for vegetal gums and mucilages; proteases which hydrolyze proteins (gelatins and caseins). Triglycerides such as lipases of the pancreatic type, attacking glycerides themselves in hydrolyzing fat, are not part of the field of enzymes used in the processing of non-glyceridic compounds.

Given the complexity of the non-glyceridic residues of certain oils and fats and the specificity of action typical for enzymes, we may use several enzymes together. Besides, it often happens that commercial "enzymes" whether of animal, vegetal or microbiological origin, actually contain several enzymes with different specific actions. Thus, for example, papain and ficine, products extracted from papaya and fig fruits, contain at the same time proteases, phosphatases

and peroxidases. Equally, it will be necessary to avoid using, for oils and fats, enzyme complexes of which some may have negative effects, for example, by producing oxidations or hydrolyses in the oil or fat itself.

According to the invention, since the processing techniques of oils and fats may be obtained enzymatically, there are three types of hydrolysis and/or depolymerization of the non-glyceridic compounds contained by them:

1) The addition and mixture in oils and fats of an enzyme or enzyme complexes previously dissolved in a small quantity of appropriate solvent (for example water). A certain number of solvents are possible, but a non-toxic and suitable solvent for the enzyme is chosen. This addition may be done in processes with successive loads, as well as in continuous processes. The quantity of enzyme(s) necessary to be added to oils and fats, according to this process, may range, depending on the enzymes and the products to be processed, from 20 to 400 ppm, i.e., from 0.02 kg to 0.4 kg of enzyme for 1000 kg of oil or fat, and preferably from 20 to 100 ppm, i.e., from 0.02 to 0.1 kg of enzyme for 1000 kg of oil, these values being understood to be for concentrated enzymes, i.e., without diluent or solvent.

2) Passage of the oil or fat through a fixed or insoluble filtering bed of enzyme(s)

on solid or semi-solid supports, preferably presenting a porous or fibrous structure. In this technique, the enzymes are trapped in the micro-cavities of the porous or fibrous structure of the supports. These consist, for example, of resins or synthetic polymers, cellulose carbonates, gels such as agarose, filaments of polymers or copolymers with porous structure, trapping small droplets of enzyme in solution in their cavities. Concerning the enzyme concentration, it is possible to go up to the saturation of the supports.

3) Dispersion of the oils and fats in the form of fine droplets, in a diluted enzymatic solution, preferably containing 0.2 to 4% in volume of enzyme. This technique is particularly described in Belgian patent No. 595,219. A cylindrical column with a height of several meters, with conical lid, is filled with a diluted enzymatic solution. For this purpose, a solvent that is non-toxic and non-miscible in the oil or fat to be processed, preferably water, is chosen. The bottom of the column is equipped with a distribution system in which the oil or fat is continuously injected in an extremely divided form (approximately 10,000 flux per m^2). Thus an infinite number of droplets of oil or fat are formed, which slowly rise in the solution of

enzymes and meet at the surface, to be evacuated continuously at the top of the conical lid of the reactor.

In all these techniques, it is important to respect the concentration, temperature and pH conditions which allow the enzyme to give its maximum catalytic effect. For this purpose, according to the invention, the enzymatic reaction takes place at a temperature between 10° and 90°C, and preferably at a temperature between 25° and 55°C, and at a pH on the order of 1 to 7. This is particularly important for concrete fats, for which the enzymes chosen are stable at the temperature at which the fat is totally melted. Generally, the enzymatic reaction is left to run for a period of time that allows obtaining practically total hydrolysis and/or depolymerization of the non-glyceridic compounds contained in the oil or fat. At the end of the operation, or during a subsequent stage, the enzymatic effect is necessarily stopped by addition of an inhibitor or simply by heat, for example by heating to a temperature of at least 85°, to the extent that the enzymatic reaction could continue in a non-desirable manner (for example with an oxidizing or hydrolyzing effect on the oils and fats themselves).

According to the invention, a typical example of application of the process for the treatment of the non-lyceridic compounds of oils and fats by addition of enzymes is the pectinase treatment

of raw palm oil, to allow for its crystallization and fractionation without undergoing the usual refining operations.

Indeed, in the last twelve years, palm oil fractionation by crystallization has become very important in the treatment of this oil. More than one quarter of the palm oil produced worldwide - estimated at 4,682 thousand tons for 1980-81 - J.A.O.C.S. January 1981) is marketed in the form of its liquid and concrete fractions. In Malaysia, more than 30 industrial plants work in palm oil fractionation. In Indonesia, 3 plants are enough to treat by fractionation half of the country's palm oil production. But all these palm oil fractionation shops are installed in oil refineries, as one of the stages in refining operations. Currently, none is installed in the oil shops of the plantations that produce raw palm oil. The reason is that, although the crystallization of a refined oil is relatively easy, it is extremely unsatisfactory and often impossible for raw palm oil.

The reason is that, in addition to free fatty acids, raw palm oil contains phosphatide and non-lipidic compounds, globally named "mucilages" or "gums" which, although apparently not very significant (0.2 to 1% of the raw oil), have a decisive negative effect on the crystallization

of raw oil. This is why, before any other operation, raw palm oil generally undergoes prior "degumming." This degumming generally consists of attacking the raw oil with a concentrated solution of phosphoric acid (0.05 to 0.2% in volume), which more or less attacks the gums precipitating them so as to retain them during subsequent filtration on active soil.

But the degumming of raw palm oil by phosphoric acid has numerous shortcomings. If one is not careful, concentrated phosphoric acid (85%) also attacks the oil itself, causing partial degradation of the oil by formation of phosphate residues. In addition, before any other operation, the precipitates formed in the oil must necessarily be filtered and retained by a sufficient quantity of active soil, causing a new loss of oil, since the soil retains oil up to 40% of its own weight. Palm oil so treated with soil undergo significant decoloration, which makes it impossible to consider it raw oil, often with significant impact on the customs duties of importing countries (in 1981, the difference in duties in the EEC is 10% of the value of the imported palm oil). Finally, phosphoric acid gives the treated oil a mineral acidity which is extremely bothersome, or even inhibiting for crystallization. This is why certain processes "neutralize" the traces of phosphoric acid which have not reacted in the oil, for

example by alkaline hydroxides or calcium carbonate. But this neutralization has the shortcoming of creating sodium or calcium soaps, which are powerful crystallization inhibitors. Consequently, these soaps must also be retained on active soil, with the shortcomings described above.

The treatment of raw palm oil with enzymes avoids the aforementioned shortcomings. Enzymes gave an absolutely specific action on the oil: pectinase, for example, will selectively hydrolyze pectins, numerous in raw palm oil, especially since the introduction of continuous, high yield presses in oil shops, which extract part of the components of vegetal fibers with the oil. Enzymes have the huge advantage of acting on the oils, which are delicate biological compounds, without violent acidification and at exceptionally moderate temperatures, since enzymes are active at temperatures quite close to ambient temperatures. Enzymes leave in place, in raw palm oil, all its characteristics of raw oil and allow for its fractionation without loss of matter, in the oil shop, without all the equipment which requires the significant investments and production expenses of the oil refinery.

To illustrate the invention more specifically, two examples of treatment, one with phosphoric acid (comparative example 1) and the other according to the invention (example 1) on commercial

palm oil, with 4.94% free fatty acids and an iodine index of 52.98, are given below.

Comparative example 1.

In a first stage, this palm oil is subjected to 14 successive fractionation tests, either as is or after various treatments, such as centrifugation, washing, attack with phosphoric acid and partial decoloration with active soil (2% Tonsil FF optimum), but always avoiding the neutralization of the oil. All these tests have been negative, since the crystals formed are extremely small (0.02 to 0.15 mm in diameter), shapeless and without consistency, in a very viscous liquid suspension.

Example 1.

According to the invention, the following test is conducted:

A - Enzyme treatment:

A charge of 30 kg of raw palm oil is heated to +50°C. We prepare 1% solutions in distilled water of Celluclast 2.0L typex enzymes (cellulase) and Ultrazym 100 (pectinase) and we add 600 g of each of these aqueous solutions to the oil, under strong agitation for a few minutes. The oil is then kept at +50°C under moderate agitation, for a total reaction time of two hours. Then, we raise the temperature to +90°C to deactivate the enzymes and prepare the mixture for filtration. The oil is dried under vacuum and filtered with a filtering aid (Celatom).

B - Fractionation:

Raw palm oil treated with enzymes is subjected to normal crystallization by heating to 68°C, followed by controlled cooling. We obtain excellent crystallization, with mostly firm rounded crystals with a diameter of 0.5 to 0.9 mm, with a few average or small crystals. Then filtered on a filter under vacuum, the oil so crystallized was filtered in 16 to 22 seconds, leaving a very dry stearin cake 12-mm thick and very liquid, shiny olein. Crystallization tests were repeated several times with the same success.

For this purpose, one must compare the enclosed figures 1 and 2 which represent, respectively, the photographs taken with the stereoscope under polarizing light, respectively of the crystals obtained according to comparative example 1 (enlargement 30 x) and the crystals obtained according to example 1 of the invention (enlargement 20 x).

It is self-understood that the invention is not limited to the embodiments described and that many modifications can be considered without leaving the scope of this patent.

Indeed, given the large number of oils and fats containing non-glyceridic compounds which may be usefully hydrolyzed or depolymerized to improve their performance during treatment by centrifugation, filtration and clarification, and also given the large number of enzymes whose

specific action may be useful for the same purpose, it is obvious that the examples could be greatly expended, each of the oils and fats and each of the enzymes being an illustrative case. Thus, oils and fats, such as chicken fat, karite butter, illipe butter, salfat and cottonseed oil could also be treated by the process of the invention.

CLAIMS

1. Process for the treatment of an oil or fat, animal or vegetal, raw, semi-processed or refined, characterized by the fact that it consists of adding to such oil or fat at least one enzyme that allows hydrolyzing and/or depolymerizing the non-glyceridic compounds contained therein.

2. Process according to claim 1, characterized by the fact that the enzyme is added before centrifugation, crystallization, fractionation, winterization or clarification of said oil or fat.

3. Process according to either one of claims 1 and 2, characterized by the fact that the enzyme is chosen from the group including phosphatase, pectinase, cellulase, amylase, gummase, protease and mixtures of two or several of these substances.

4. Process according to either one of claims 1 to 3, characterized by the fact that the aforementioned treatment is done by adding the enzyme dissolved in the form of a solution in a non-toxic solvent, under intense agitation conditions.

5. Process according to claim 4, characterized by the fact that the quantity in weight of the enzyme per 1,000 kg of oil or fat ranges between 0.02 and 0.4 kg.

6. Process according to claim 5, characterized by the fact that the quantity in weight

of enzyme per 1,000 kg of oil or fat ranges between 0.02 and 0.1 kg.

7. Process according to either one of claims 1 to 3, characterized by the fact that the aforementioned treatment is done by passing the oil or fat over a filtering enzyme bed fixed on a solid or semi-solid support.

8. Process according to claim 7, characterized by the fact that the support presents a porous or fibrous structure.

9. Process according to either one of claims 1 to 3, characterized by the fact that the aforementioned treatment is done by dispersion of the oil or fat in the form of fine droplets, in a diluted enzymatic solution, the solvent used for this purpose being non-toxic and non-miscible in said oil or fat.

10. Process according to claim 9, characterized by the fact that the enzymatic solution contains 0.2 to 4% in volume of enzyme.

11. Process according to either one of claims 1 to 10, characterized by the fact that the enzymatic reaction is allowed to continue for a period of time which allows obtaining the practically total hydrolysis and/or depolymerization of non-glyceridic compounds.

12. Process according to either one of claims 1 to 11, characterized by the fact that the enzymatic reaction takes place at a temperature ranging between 10° and 90°C and a pH of 1 to 7.

13. Process according to claim 12, characterized by the fact that the enzymatic reaction takes place at a temperature ranging between 25° and 55°C.

14. Process according to either one of claims 11 to 13, characterized by the fact that, after the practically total hydrolysis and/or depolymerization of non-glyceridic compounds, the enzyme-treated fat or oil is heated to a temperature of at least 85°C, adding an inhibiting substance, so as to deactivate the enzyme or enzymes.

Fig. 1

Fig. 2